Crystal structure of pentachloro(3,3'-thiodipropionitrile)tantalum(V), $\text{TaCl}_5[\text{NC}(\text{CH}_2)_2\text{S}(\text{CH}_2)_2\text{CN}]$ and of pentachloro(3,3'-thiodipropionitrile)niobium(V), $\text{NbCl}_5[\text{NC}(\text{CH}_2)_2\text{S}(\text{CH}_2)_2\text{CN}]$

Ibrahim-Abdelhalim-Ahmed, R. Blachnik, H. Reuter and K. Stumpf

Universität Osnabrück, Institut für Chemie, Barbarastr. 7, D-49069 Osnabrück, Germany

Received August 12, 1998, CSD-No. 409362 and CSD-No. 409363

Abstract

$\text{C}_6\text{H}_8\text{Cl}_5\text{N}_2\text{STa}$, monoclinic, $P12_1/n1$ (No. 14), $a = 8.051(3) \text{ \AA}$, $b = 9.430(2) \text{ \AA}$, $c = 18.293(5) \text{ \AA}$, $\beta = 100.32(3)^\circ$, $V = 1366.4 \text{ \AA}^3$, $Z = 4$, $R_g(F) = 0.031$, $R_w(F^2) = 0.073$, $T = 223 \text{ K}$.

$\text{C}_6\text{H}_8\text{Cl}_5\text{N}_2\text{NbS}$, monoclinic, $P12_1/n1$ (No. 14), $a = 8.069(1) \text{ \AA}$, $b = 9.4689(9) \text{ \AA}$, $c = 18.440(2) \text{ \AA}$, $\beta = 100.19(1)^\circ$, $V = 1386.7 \text{ \AA}^3$, $Z = 4$, $R_g(F) = 0.020$, $R_w(F^2) = 0.057$, $T = 293 \text{ K}$.

Source of material

The title compounds were prepared using standard Schlenk techniques. Niobium(V) chloride or tantalum(V) chloride and 3,3'-thiodipropionitrile were dissolved in dichloromethane. The solution was covered with a layer of n-hexane. Solvent diffusion occurred at room temperature over a period of days and resulted in yellow and red crystals for niobium(V) chloride and tantalum(V) chloride, respectively. Both compounds are sensitive to moisture.

Discussion

Structure data reveal that both compounds are isotypic with almost the same bond lengths and bond angles. The ligand molecule coordinates via only one nitrogen atom ($d(\text{Nb}-\text{Cl}) = 2.249 \text{ \AA}$, $d(\text{Nb}-\text{N}) = 2.259 \text{ \AA}$; $d(\text{Ta}-\text{Cl}) = 2.232 \text{ \AA}$, $d(\text{Ta}-\text{N}) = 2.239 \text{ \AA}$). The neutral complex is a distorted octahedra centred with the metal atom. Due to the high moisture sensitivity other investigation methods such as D.S.C. could not be applied. The first complexes between niobium(V) and tantalum(V) halides with dinitriles have been reported in [1].

1. Pentachloro(3,3'-thiodipropionitrile)tantalum(V), $\text{TaCl}_5[\text{NC}(\text{CH}_2)_2\text{S}(\text{CH}_2)_2\text{CN}]$

Table 1. Data collection and handling.

Crystal:	yellow needle, size 0.31 x 0.46 x 0.86 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	91.44 cm^{-1}
Diffractometer, scan mode:	Siemens P4, $2\theta/\omega$
$2\theta_{\text{max}}$:	50°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	3325, 2411
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 1914
$N(\text{param})_{\text{refined}}$:	138
Programs:	SHELXS-86 [2], SHELXL-93 [3]

Table 2. Atomic coordinates and displacement parameters (in $\text{\AA}^2$).

Atom	Site	x	y	z	U_{iso}
H(31)	4e	0.6586(9)	0.3128(7)	0.1745(4)	0.040(9)
H(32)	4e	0.7872(9)	0.4072(7)	0.2284(4)	0.040(9)
H(41)	4e	1.003(1)	0.3305(8)	0.1573(4)	0.040(9)
H(42)	4e	0.872(1)	0.2178(8)	0.1195(4)	0.040(9)
H(61)	4e	1.044(1)	0.3467(7)	0.3134(4)	0.040(9)
H(62)	4e	1.136(1)	0.2132(7)	0.3523(4)	0.040(9)
H(71)	4e	1.245(1)	0.3668(7)	0.2370(4)	0.040(9)
H(72)	4e	1.334(1)	0.3707(7)	0.3205(4)	0.040(9)

Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Ta(1)	4e	0.73978(3)	0.75545(3)	0.00680(2)	0.0174(2)	0.0185(2)	0.0185(2)	−0.0004(1)	−0.0005(1)	0.0013(1)
Cl(1)	4e	0.4494(2)	0.7692(2)	−0.0012(1)	0.0193(9)	0.046(1)	0.032(1)	0.0061(8)	0.0003(8)	−0.0026(9)
Cl(2)	4e	1.0243(2)	0.6998(2)	0.0298(1)	0.0168(9)	0.050(1)	0.041(1)	0.0006(8)	0.0010(8)	0.000(1)
Cl(3)	4e	0.6943(2)	0.5838(2)	−0.0864(1)	0.033(1)	0.0318(9)	0.030(1)	0.0003(8)	0.0019(8)	−0.0089(8)
Cl(4)	4e	0.7741(3)	0.8908(2)	0.1142(1)	0.042(1)	0.037(1)	0.031(1)	−0.0055(9)	0.0008(9)	−0.0119(8)
Cl(5)	4e	0.7651(3)	0.9380(2)	−0.0702(1)	0.068(2)	0.032(1)	0.044(1)	0.002(1)	0.015(1)	0.0160(9)
N(1)	4e	0.7260(8)	0.5732(6)	0.0839(4)	0.025(3)	0.021(3)	0.038(4)	0.001(3)	0.003(3)	0.005(3)
C(2)	4e	0.7370(9)	0.4834(7)	0.1240(4)	0.019(4)	0.018(3)	0.037(4)	0.000(3)	0.005(3)	0.002(3)
C(3)	4e	0.7615(9)	0.3681(7)	0.1786(4)	0.025(4)	0.025(4)	0.024(4)	0.000(3)	−0.001(3)	0.009(3)
C(4)	4e	0.908(1)	0.2716(8)	0.1647(4)	0.027(4)	0.030(4)	0.019(4)	0.001(3)	−0.002(3)	0.001(3)
S(5)	4e	0.9776(2)	0.1505(2)	0.2399(1)	0.029(1)	0.0228(9)	0.038(1)	−0.0013(8)	−0.0017(9)	0.0047(8)
C(6)	4e	1.108(1)	0.2631(7)	0.3053(4)	0.027(4)	0.026(4)	0.025(4)	0.003(3)	0.000(3)	−0.001(3)
C(7)	4e	1.273(1)	0.3104(7)	0.2819(4)	0.030(4)	0.018(3)	0.038(4)	−0.002(3)	−0.001(4)	−0.007(3)
C(8)	4e	1.382(1)	0.1940(9)	0.2684(4)	0.027(4)	0.033(4)	0.033(4)	−0.003(4)	−0.001(3)	−0.007(4)
N(9)	4e	1.4657(9)	0.1038(8)	0.2580(5)	0.034(4)	0.043(5)	0.074(6)	0.008(4)	0.000(4)	−0.021(4)

2. Pentachloro(3,3'-thiodipropionitrile)niobium(V), NbCl₅(NC(CH₂)₂S(CH₂)₂CN]

Table 4. Data collection and handling.

Crystal:	light red needle, size 0.06 x 0.03 x 0.23 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	19.51 cm ^{−1}
Diffractometer, scan mode:	Siemens P4, 2 θ / ω
2 θ _{max} :	44°
$N(hkl)$ _{measured} , $N(hkl)$ _{unique} :	2330, 1608
Criterion for I_{obs} , $N(hkl)$ _{gt} :	$I_{obs} > 2 \sigma(I_{obs})$, 1524
$N(param)$ _{refined} :	138
Programs:	SHELXS-86 [2], SHELXL-93 [3]

Table 5. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U _{iso}
H(3A)	4e	0.7899(4)	1.0927(3)	0.2280(2)	0.048(3)
H(3B)	4e	0.6604(4)	1.1857(3)	0.1748(2)	0.048(3)
H(4A)	4e	0.8686(4)	1.2790(3)	0.1193(2)	0.048(3)
H(4B)	4e	1.0001(4)	1.1676(3)	0.1566(2)	0.048(3)
H(6A)	4e	1.1361(4)	1.2872(3)	0.3505(2)	0.048(3)
H(6B)	4e	1.0446(4)	1.1536(3)	0.3129(2)	0.048(3)
H(7A)	4e	1.3324(4)	1.1303(3)	0.3203(2)	0.048(3)
H(7B)	4e	1.2439(4)	1.1315(3)	0.2375(2)	0.048(3)

Table 6. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Nb(1)	4e	0.73968(3)	0.74242(2)	0.00664(2)	0.0300(2)	0.0274(2)	0.0274(2)	0.0000(1)	0.0004(1)	−0.0020(1)
Cl(1)	4e	0.4506(1)	0.73148(9)	−0.00042(5)	0.0324(5)	0.0658(6)	0.0505(6)	−0.0092(4)	0.0002(4)	0.0071(4)
Cl(2)	4e	1.0233(1)	0.7988(1)	0.03008(5)	0.0295(4)	0.0684(6)	0.0557(6)	−0.0008(4)	0.0015(4)	−0.0002(5)
Cl(3)	4e	0.6956(1)	0.91499(8)	−0.08519(4)	0.0472(5)	0.0452(5)	0.0423(5)	−0.0001(4)	0.0037(4)	0.0126(4)
Cl(4)	4e	0.7727(1)	0.60865(9)	0.11349(5)	0.0635(6)	0.0512(5)	0.0434(5)	0.0079(4)	0.0040(4)	0.0166(4)
Cl(5)	4e	0.7652(1)	0.56155(9)	−0.06966(5)	0.0966(8)	0.0449(5)	0.0582(6)	0.0012(5)	0.0182(5)	−0.0216(4)
N(1)	4e	0.7253(3)	0.9254(3)	0.0839(1)	0.037(2)	0.033(1)	0.033(1)	0.001(1)	−0.000(1)	−0.008(1)
C(2)	4e	0.7372(4)	1.0145(3)	0.1249(2)	0.030(2)	0.040(2)	0.038(2)	0.002(1)	0.001(1)	0.001(2)
C(3)	4e	0.7632(4)	1.1309(3)	0.1785(2)	0.036(2)	0.037(2)	0.037(2)	−0.001(1)	0.004(1)	−0.013(1)
C(4)	4e	0.9060(4)	1.2260(3)	0.1642(2)	0.042(2)	0.043(2)	0.033(2)	−0.003(1)	−0.002(2)	−0.002(1)
S(5)	4e	0.9770(1)	1.34832(8)	0.23837(5)	0.0390(5)	0.0307(4)	0.0498(5)	0.0004(3)	−0.0037(4)	−0.0060(3)
C(6)	4e	1.1087(4)	1.2366(3)	0.3043(2)	0.043(2)	0.043(2)	0.031(2)	−0.004(1)	−0.001(2)	−0.002(1)
C(7)	4e	1.2709(4)	1.1891(3)	0.2815(2)	0.040(2)	0.036(2)	0.045(2)	−0.000(2)	−0.002(2)	0.004(2)
C(8)	4e	1.3785(4)	1.3039(4)	0.2671(2)	0.036(2)	0.043(2)	0.046(2)	0.004(2)	−0.006(2)	0.006(2)
N(9)	4e	1.4634(4)	1.3932(4)	0.2561(2)	0.047(2)	0.064(2)	0.095(3)	−0.008(2)	0.000(2)	0.022(2)

References

- Gill, M. S.; Ahuja, H. S.; Rao, G. S.: Complexes of Niobium(V) and Tantalum(V) Halides with Dinitriles, 1, Malonitrile und Succinonitrile. *Inorg. Chim. Act.* **7** (1973) 359–364.
- Sheldrick, G. M.: SHELXS-86. Program for crystal structure determination. University of Göttingen, Germany 1986.
- Sheldrick, G. M.: SHELXL-93. Program for crystal structure refinement. University of Göttingen, Germany 1993.